

Centro Para Prevenção da Poluição (C3P)
Engineering and Technical Services

Potential Alternatives Report

C3P.Proj.CS.Port.001

For the Replacement of a Chromate and
High-VOC Coating System in Aircraft
Painting Process

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PREFACE

This report was prepared by the Centro Para Prevenção da Poluição (C3P) under the guidance of the NASA Acquisition Pollution Prevention Office. This report was prepared in accordance with the tenants of the *Joint Statement (JS) between NASA and the Portuguese Ministry of the Environment Regarding Cooperation in the Field of Environmental Pollution Prevention*, signed by the American Ambassador and the Ministério das Cidades, Ordenamento do Território e Ambiente Portugal, and the subsequent *Terms of Reference (TOR)*, signed by the NASA Director of Environmental Management, Portuguese President of the Institute of Environment, and the C3P Director General on September 18, 2002. The structure, format, and depth of technical content of the report was determined by a joint project team comprised of representatives from C3P, Instituto de Soldadura e Qualidade (Institute of Welding and Quality) (ISQ), International Trade Bridge, Inc. (ITB), Instituto de Engenharia Mecânica e Gestão Industrial (Institute of Mechanical Engineering and Industrial Management) (INEGI), TAP Portugal, and OGMA – Indústria Aeronáutica de Portugal, S.A..

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EXECUTIVE SUMMARY

A common coating system on aluminum substrates consists of a chromate conversion coating, a primer and a topcoat.

Chrome conversion coating involves the treatment of a metal substrate with a chrome solution to produce an adherent coating. The metal substrate is changed to a layer of chromium salts to produce the desired decorative or functional properties. Chrome conversion coatings are used for three general purposes:

- Increase corrosion resistance
- Improve paint (primer) adhesion
- Minimize electrical resistance.

Chrome primers are commonly applied to surfaces as a protective coating offer significant corrosion protection.

Although chrome conversion coating and primer coatings offers many advantageous coating properties, its use of hexavalent chromium is strictly regulated due to the compound's toxicity and suspected carcinogenicity. For this reason, manufacturers have begun to identify, evaluate, and implement acceptable alternatives for chrome conversion coating and primer coating where feasible. These alternative technologies commonly generate less pollution than chrome conversion coatings and chrome primers, and have fewer associated health and safety risks.

Also traditional coatings are paints containing high amounts of volatile organic compounds (VOC), such as methyl ethyl ketone, toluene, and xylene, and some percentage of solid components. Alternative coatings seek to reduce the amount of VOCs, and yet retain or improve the ability of the coating to protect metallic or composite surfaces.

At TAP Portugal, and OGMA – *Indústria Aeronáutica de Portugal, S.A.*, chrome in chemical conversion coatings and primers coatings, as well as VOC found in paints, were identified as a hazardous material of concern, and targeted for elimination or reduction.

This Potential Alternatives Report (PAR) provides an analysis of identified alternatives to chromate and high-VOC coating systems and recommended alternatives for testing and possible implementation at TAP and OGMA.

Two viable alternatives have been identified. These viable alternatives are *High Solids Painting Scheme* from Akzo Nobel; and *PreKote Surface Pretreatment*, from Pantheon Chemical, plus the *High Solids Painting Scheme*, from Akzo Nobel. The environmental, safety, and occupational health characteristics of these viable alternatives were evaluated. In addition, the key process characteristics of

these alternatives were compared to those of the existing process. As a result of the analyses, both of the alternatives were classified as potential alternatives and chosen for testing/performance comparison in accordance with the approved Joint Test Protocol (JTP), *Joint Test Protocol for the Replacement of a Chromate and High-VOC Coating System in Aircraft Painting Process*, dated November, 2004. A Joint Test Report (JTR) will document the data and results of the testing/performance comparison to minimize duplication of effort.

Comment [JVP1]: Confirm date

INTRODUCTION

The National Aeronautics and Space Administration (NASA) and the Portuguese Ministry of Urban Affairs, Spatial Planning and the Environment, in their concern for the quality of the natural environment have agreed jointly to explore ways to prevent environmental pollution.

The following outlines specific areas of pollution prevention (P2) interests in the joint cooperation between NASA and the Portuguese Ministry of Environment:

- Integrating environmental, safety, and occupational health considerations in acquisition, manufacturing, and maintenance processes/procedures;
- Information sharing on integrating environment, safety, and occupational health considerations into life cycle analysis;
- Use of existing information networks for environmental purposes;
- Information sharing programs on United States and European regulations and their potential impact on manufacturing and maintenance processes and their impacts on operational capability/supportability; and
- Integrating safety and occupational health considerations into environmental programs.

The NASA Acquisition Pollution Prevention (AP2) Program Office, operated under the Spaceport Technology Directorate (YA) at Kennedy Space Center, Florida, will act as facilitator while the Center for Pollution Prevention (C3P), in Lisbon, Portugal, will establish the infrastructure and develop strategic plans - The C3P Mission is to identify and validate pollution prevention technologies through joint activities that enhance environmental stewardship and reduce risk while minimizing duplication of effort and associated costs.

To reduce HazMats, the C3P process first identifies the HazMat, related process, and affected substrates or parts. Details identified include equipment requirements; material and energy usage; waste and emission generation; environmental, safety, and occupational health (ESOH) issues; and capital and operating costs.

Identifying and selecting alternative processes that have the potential to reduce the identified HazMats can be a complicated task due to the fast pace at which new technologies emerge and the ever-increasing volume of published and unpublished documentation. Under the C3P process, a technology survey is performed to identify commercially available or near commercially available alternative technologies. The alternatives are identified through literature searches, electronic database searches, Internet searches, customized surveys, and/or personal and professional contacts.

After reviewing technical and ESOH information in the technology survey,

technical representatives select a shortened list of viable alternative technologies. The selection rationale and conclusions are documented in the PAR, and vendors of the selected technologies are contacted concerning their specific products.

The identified vendor products then undergo a more in-depth technical and preliminary ESOH analysis. The technical analysis includes determining how well the alternatives match the current operations and future needs. Examples of evaluation criteria may include expected additional equipment, material and energy usage, waste and emission generation, and capital and operating costs.

After reviewing the technical and ESOH analyses, technical representatives select potential alternatives for testing in accordance with the *C3P Joint Test Protocol for the Replacement of a Chromate and High-VOC Coating System in Aircraft Painting Scheme*, dated November, 2004. Test results will be reported in the JTR.

Comment [JVP2]: Confirm date

Table 1 summarizes the target HazMat, process and material and affected programs at TAP Portugal.

Table 1. Target HazMat Summary – TAP		
Target HazMats	Process/Material	Affected Programs
Hexavalent Chrome	Chemical Conversion Coatings	<u>Airbus:</u> A310, A320 family and A340
Volatile Organic Compounds	Primers	<u>Boeing:</u> B727, B737
	Topcoats	<u>Lockheed:</u> L1011

1. BASELINE PROCESS

The following baseline information was provided by TAP.

The painting systems should comply with the Aerospace Material Specification AMS 3095 Paint, Gloss, Airline Exterior System of SEA International (Annex A).

Airbus Industries defines two procedures of product application related with exterior painting process. These documents are designated by *Process and Material Specifications* (PMS), and are PMS 01-02-29 and PMS 01-02-27.

PMS 01-02-29 defines the tests that should be performed after the painting process is completed, for both primers and topcoats. These tests are adhesion and thickness. For thickness tests the proper equipment to be used is the Isometer or Permascope for light alloys and Microtest equipment for steels. For the adhesion tests it should be used scotch tape 250 from 3M (adhesive tape) in different points of the painted surface. In the test coupons the thickness measurement should be done before the adhesion test. If necessary these coupons can be used for verification of the decoration paint colour. In this procedure, is also defined as a criterion of aircraft exterior painting approval, the evaluation of painting conditions, based on technical and aesthetics aspects. Concerning the technical aspects, it should be considered the protection factor of the painting system, while the aesthetics aspects are related with the manufacturer and operator image.

The PMS 01-02-27 defines primer application. The point 3.2.4 of the PMS 01-02-27 document specifies thickness and weight (by surface unit) range values, which epoxy and polyurethane based dry films should have. The values of thickness and weight, by surface unit, are respectively, $17 \pm 3\mu\text{m}$ and 30g/m^2 . In the quality requirements it is specified that visual inspections should be done at 100%, for search of irregularities. After drying the thickness measurements should be done using non-destructive methods. The equipment to be used should be Microtest, Isometer, Permascope, or Elcometer. The adhesion test should be conducted, as follows:

- Degrease the test area.
- Apply adhesive tape on the clean area. Use Scotch tape N°250 with 1 inch of width, with no longer than 12 months after manufacture date. It should be assured that there is a perfect contact between the adhesive tape and the coating avoiding air bubble imprisonment.
- Remove the tape in an abrupt movement keeping an angle of approximately 90° .

If the adhesion test fails the piece should be rejected.

1.1. Baseline Process Flow

The sequence of steps for painting preparation is shown in Figure 1.

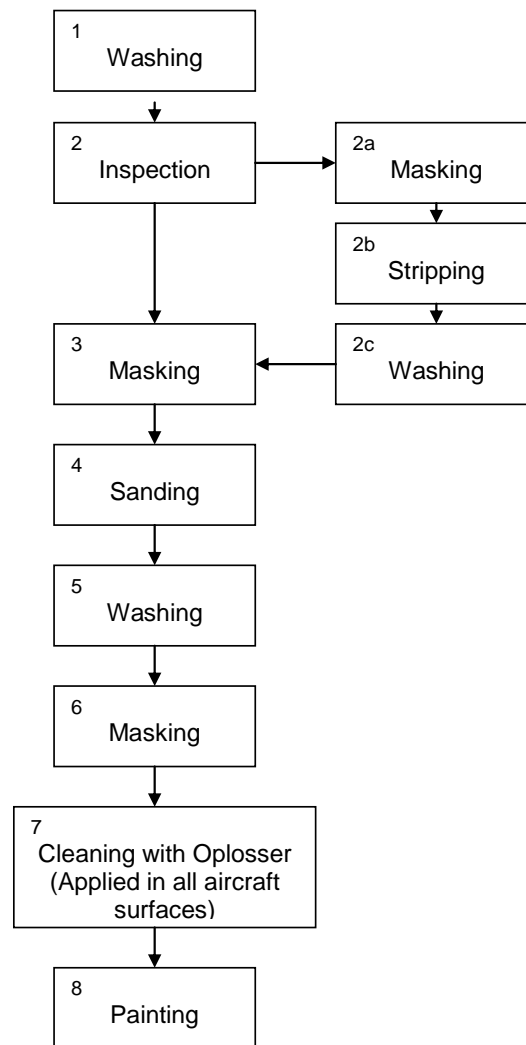


Figure 1. Steps for painting preparation

Figure 2 shows the sequence of steps for TAP baseline painting process.

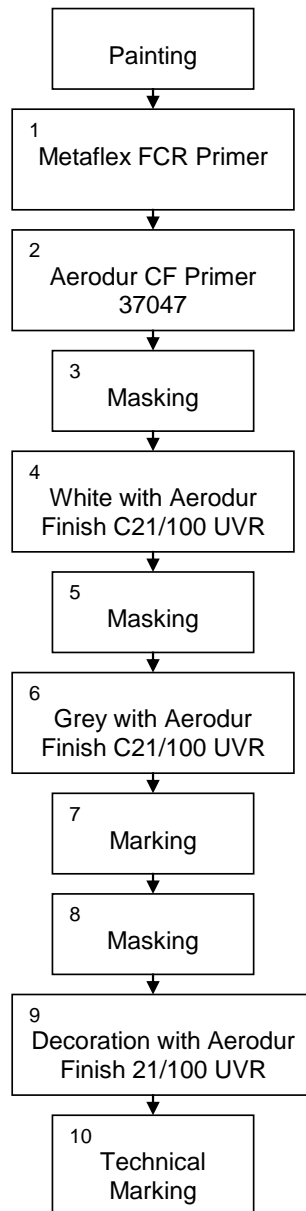


Figure 2. Steps for baseline painting process

1.2. Baseline Process Description

Previous to the painting process it's required a preparation of all aircraft surfaces. Initially, all surfaces are washed with cold water, followed by an inspection. If the surface is not in perfect conditions it's necessary to mask, followed by a stripping process and wash with cold water. If the surface is in perfect conditions is conducted masking, followed by sanding, washing with cold water and masking again. After masking, all aircraft surfaces are cleaned with *Oplosser*.

The following describes each step of TAP's painting process:

1. *Application of Metaflex FCR Primer*: Metaflex FCR Primer is a 3-component filiform corrosion resistance washprimer and is spray gun applied in the areas with bare metal.
2. *Application of Aerodur CF Primer 37047*: Aerodur CF Primer 37047 is a 3-component chromate cured modified epoxy primer for exterior use and is spray gun applied in all aircraft surfaces.
3. *Masking*: fuselage lower half.
4. *White with Aerodur Finish C21/100 UVR*: Aerodur Finish C21/100 UVR is an universal 3-component, high gloss very durable polyurethane finish for interior and exterior use, and is spray gun applied in the fuselage upper half.
5. *Masking*: fuselage upper half.
6. *Grey with Aerodur Finish C21/100 UVR*: spray gun application in fuselage lower half.
7. *Marking*
8. *Masking*
9. *Decoration with Aerodur Finish C21/100 UVR*: spray gun application in accordance with TAP's painting draw.
10. *Technical Marking*

1.3. Baseline Process Equipment

The baseline equipment for the painting process is listed below:

- Thermohygrometer
- Flow cup
- Chronometer
- Mechanical Shaker
- Thickness gauge
- Gloss gauge
- Spray guns and pumps (See Table 2).

Table 2. Spray Guns and Pumps used in the Baseline Painting Process	
Product	Equipment
<i>Metaflex FCR Primer</i>	High pressure electrostatic spray guns model 4000 with Monarch pumps
<i>Aerodur CF Primer 37047</i>	High pressure electrostatic spray guns model 4000 with Monarch pumps
<i>Aerodur Finish C21/100 UVR</i>	High pressure electrostatic spray guns model 4500 with Monarch pumps

1.4 Baseline Material and Energy Usage

The painting system products used at TAP are *Metaflex FCR Primer*, *Aerodur CF Primer 37047* and *Aerodur Finish C21/100 UVR*, all from Akzo Nobel.

Metaflex FCR Primer is a 3-component filiform corrosion resistance washprimer which has been designed as an alternative pre-treatment to chemical conversion coatings; for reactivation of aged anodized or chromated alloys and sealed anodized surfaces; for stippability of polyurethane systems with alkaline paint removers; and to provide adhesion of subsequent polyurethane or epoxy/isocyanate primers.

Aerodur CF Primer 37047 is a 3-component chromate free isocyanate cured modified epoxy primer for exterior use.

Aerodur Finish C21/100 UVR is a universal 3-component, high gloss very durable polyurethane finish for interior and exterior use.

The specifications respected by the painting system products are shown in Table 3.

Table 3. Specifications of the Baseline Painting System Products	
Products	Specifications
Metaflex FCR Primer	AIMS 04.04.012 (TN 10.113) BMS 10-72 Type V FSD 7065 Airbus CML No. 16-020 A
Aerodur CF Primer 37047	SMI 70043 STD 175437
Aerodur Finish C21/100 UVR	AIMS 04.04.012 BAEP 3545 BMS 10-72 Type V DOL 256 MEP 10-61 SMI 70089-1

	Airbus CML No. 07-017 Airbus CML No. 16-016
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Note: Specification Codes: AIMS-Airbus Industrie Material Specification, BMS-Boeing Material Specification, Airbus CML-Airbus Consumable Material List, BAMS Bombardier Aerospace Material Specification, MEP-Embraer Specification, FSD Swedish Defense Specification, SMI-Air France Specification, STD-Saab Specification, BAEP-BAE Systems Specification and DOL-Fairchild Dornier Specification.

The composition and information on ingredients of the baseline painting products are described in the following Table.

Table 4. Composition and information on ingredients of Painting Products (Metaflex FCR Primer, Aerodur CF Primer 37047, Aerodur Finish C 21/100 UVR)		
Chemical	CAS No.	Percentage (%)
Metaflex FCR Primer		
Propan2-ol	67-63-0	50-75
Zinc chromates	11103-86-9	10-25
Toluene	108-88-3	1-2.5
Isobutyl acetate	110-19-0	1-2.5
Butan-1-ol	71-36-3	1-2.5
Phenol	108-95-2	0-1
Aerodur CF Primer 37047		
2-Methoxy-1-methylethyl acetate	108-65-6	10-25
n-butyl acetate	123-86-4	10-25
Phosphoric acid, zinc salt (2:3)	7779-90-0	10-25
Butan-2-ol	78-92-2	2.5-10
Solvent naphtha (petroleum), heavy arom.	64742-94-5	0-1
Zinc oxide	1314-13-2	0-1
2-Methoxypropyl acetate	70657-70-4	0-1
Aerodur Finish C 21/100 UVR		
2-Methoxy-1-methylethyl acetate	108-65-6	25-50
n-butyl acetate	123-86-4	1-2.5
Decanedioic acid, bis (1,2,2,6,6-pentamethyl-4-piperidiny) ester	41556-26-7	0-1
2-Methoxypropyl acetate	70657-70-4	0-1
Decanedioic acid, methyl 1,2,2,6,6-pentamethyl-4-piperidiny ester	82919-37-7	0-1

No data available on the energy usage.

1.5. Baseline Waste and Emissions Summary

The wastes produced in TAP Painting Area are described in Table 5 with the respective European Waste Catalogue and Hazardous Waste List (ELR) Code.

Table 5. Wastes produced in TAP Painting Area with respective ELR code	
Residue Type	ELR Code
Epoxy and polyurethane based paints and painting chamber sludge	080111
Non-halogenated solvents	140603
Painting residues with stripper	160302

The non-halogenated solvents are recycled by Ecosocer Company. The paints, sludge, and painting residues with stripper are sent to a specific dirt fill of Industrial Hazardous Wastes.

Siemens-Efacec is contracted by TAP services to collect wastes to be delivered to Quimitécnica, a waste management entity. Table 6 shows the description and wastes quantities produced by TAP Painting Area. The values refer to the quantities produced between 1998 and 2002.

Table 6. Wastes quantities produced in TAP painting area between 1998 and 2002						
ELR Code	Description	1998	1999	2000	2001	2002
080111	Epoxy and polyurethane based paints and painting chamber sludge (in tons)	1	1.5	0	3.6	0
140603	Non-halogenated solvents (in cubic meters)	11.8	21.8	14	16.6	10.6
160302	Painting residues with stripper (in tons)	-	-	-	11	16

During 2003 and 2004 the recovery, separation and classification of the wastes has been transferred from TAP-Maintenance & Engineering to TAP Services / Siemens-Efacec. These data were not included in this report due to the changes of the wastes classification.

The levels of VOC's emissions from the products of the baseline painting system were provided by the manufacturer. The data is shown on Table 7.

Table 7. Level of VOC emissions from the Baseline Painting Products	
Products	VOC (grams/liter)
Preparation for painting	
Solvent Oplosser	826
Painting	
Wash-primer	
Metaflex FCR Primer	656
Metaflex FCR Hardener	799
Intermediate Primer	
Aerodur CF Primer 37047	606
Hardener S66/14	562
Topcoat	
Aerodur Finish C21/100 UVR BAC 7067	447
Aerodur Finish C21/100 UVR BAC 707	458
Aerodur Finish C21/100 UVR BAC 701	561
Aerodur Finish C21/100 UVR BAC 1247	394
Aerodur Finish C21/100 UVR BAC 4213	512
Aerodur Finish C21/100 UVR PMS 012C	498
Aerodur Finish C21/100 UVR PMS Reflex Blue	483
Other painting products	
Hardener S66/22R	640
Thinner 98056	908
Thinner 96184	908
Thinner 98064	900
Thinner C25/90S	849

1.6 Environmental, Safety, and Occupational Health (ESOH) Status for the Baseline Process

Although chrome conversion coating offers many advantages, the use of hexavalent chromium is facing increasing regulation in both the United States and Europe due to the compound's toxicity and suspected carcinogenicity. The U.S. Environmental Protection Agency (EPA) lists chromium as one of the 17 materials that are targeted for strict regulation.

Continued use of the chrome process carries a growing risk of workplace and environmental liability, along with increased costs for trucking inventories, monitoring emissions, and reporting usage of chromium compounds and resulting wastes. These regulatory driving forces are increasing manufacturing costs and hazardous material liability, leading industry to identify, evaluate, and implement acceptable alternatives for the chrome conversion coating and chrome primers.

Coatings containing VOC are toxic to human health. In the European Union VOC emissions are regulated by EU Directive 1999/13/CE, March 11, 1999, that has the objective to reduce both the direct and indirect effects of the VOC emissions

to the environment, as well as reduce the potential risks to human health in consequence of a series of procedures applicable to the industrial activities described in the Directive.

1.6.1. Environmental Issues, Health and Safety Issues

TAP Maintenance and Engineering complies with the Portuguese National Legislation related to Hygiene and Safety issues, namely:

- Law-decree no. 441/91, November 14, altered by Law-decree no. 133/99, April 21 – Establishes the juridical regime within the scope of Safety, Hygiene and Health.
- Law-decree no. 488/99, November 17 – Defining the application forms of the juridical regime of Safety Hygiene and Health for Public Administration and revokes the Law-decree no. 191/95, July 28.
- Law-decree no. 26/94 February 1, altered by Law-decree no. 7/95, March 9, and Law-decree no. 109/2000 June 30, that republishes it, with all the modifications - Establishing the regime of organization and operation of the activities for the Safety, Hygiene and Health.

The workers in TAP Painting area are exposed to mechanical and chemical risks. Thereby TAP Maintenance and Engineering supply the workers with Individual Protection Equipment (IPE). These are intended to eyes, airways, torso and upper and lower limb protection. The equipments respect the Portuguese national legislation or in their absence, the international legislation. The legislation that regulates the IPE's is the following:

- Law-decree no. 128/93, April 22, altered by Law-decree no. 139/95 June 14, and Law-decree no. 374/98, November 24 (First article of Law-decree 374/98 revoked by Law-decree no. 320/2001). – Establishing the essential technical demands of safety that the individual protection equipment should comply, with the objective of preserving the health and the safety of its users.
- Law-decree no. 348/93, October 1, - Minimal prescriptions in terms of workers health and safety, using IPE.
- Government Directive no. 988/93, October 6 - Minimal prescriptions in terms of workers health and safety, using IPE (Regulates the Law-decree no. 348/93, October 1).
- Government Directive no. 1131/93, November 4, altered by the Government Directive no. 109/96, April 10, and by Government Directive no. 695/97, August 19 – Establishing the essential technical demands of safety that the IPE must respect, with the objective of preserving health and safety of its users.

Table 8 shows all the IPE's used by Maintenance and Engineering/Aircraft

Maintenance/Base Maintenance (ME/MA/MB) – Painting – Painting Shop
(Hangar 4, Hangar 5, Hangar 6).

Table 8. Safety equipment used in TAP painting area (ME/MA/MB) – Painting – Painting Shop (Hangar 4, Hangar 5, Hangar 6)

IPE	Type	Certification
Ultravision Glasses	Eye protection (risk factor of chemical nature)	DIN EN ISO 9001
Half-mask 3M 7500 series	Respiratory protection (risk factor of chemical nature)	EN 140:1999 CE 0086
Filter for gas and vapours ref. 6057 ABE1 for half-mask 3M series 7500 and mask 3M-6800S	Respiratory protection (risk factor of chemical nature)	EN 141:2000 CE 0086
Anti-particle pre-filter ref. 5911 P1 for half mask 3M 7500 series	Respiratory protection (risk factor of chemical nature)	EN 143 CE 0086
Full Face breathing mask 3M-6800S	Respiratory protection (risk factor of chemical nature)	EN 136 CL 1-1996 CE 0086
Anti-particle pre-filter ref. 5911 P3 for mask 3M-6800S	Respiratory protection (risk factor of chemical nature)	
Breathing mask 3M 9310	Respiratory protection (risk factor of mechanical nature - dusts)	EN 149:2001 CE 0086
Breathing mask 3M 9312	Respiratory protection (risk factor of mechanical nature - dusts)	EN 149:2001 CE 0086
Plastic arm protection	Arm protection (risk factor of chemical nature)	
Policloroprene glove Mapa Baltex TECHNIC 420	Hand protection (risk factor of chemical nature)	
Nitrilo glove Ansell Edmonton HYNIT	Hand protection (risk factor of mechanical nature)	3111 EN 388
Nitrilo glove Ansell Edmonton NITRASAFE	Hand protection (risk factor of mechanical nature)	4331 EN 388 X1XX4X EN 407 CE 0493
PVC apron	Torso protection (risk factor of chemical nature)	
Protection suite Tyvek - PRO/SHIELD 2	Body protection (risk factor of chemical nature – painting operation)	CE 0120
Protection suite KLEENGUARD reference IPP	Body protection (risk factor of chemical nature)	EN 340 CE 0120
Protection shoes with steel toecap TRUENO-LUIBA model	Feet protection (risk factor of mechanical nature)	EN 345-1 EN 347-1
Protection boots with steel toecap	Feet protection	EN 345-1

TRUENO AGUBA model	(risk factor of mechanical nature)	EN 347-1
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The IPE' accessories equipment is shown in Table 9.

Table 9. IPE's accessories list used in Painting areas	
IPE	Type
Replacement lenses for Ultravision glasses	Eye protection (risk factor of chemical nature)
Small hand towel for mask cleaning reference 3M 105	Respiratory protection (risk factor of chemical nature)
Protection pellicle for mask 3M-6800S	Respiratory protection (risk factor of chemical nature)

The Threshold Limit Values (TLV) of the painting materials were collected from the Portuguese Norm NP 1796:2004 and from the publication Threshold Values for Chemical Substances and Physical Agents of the American Conference of Governmental Industrial Hygienists (ACGIH) (See Table 10).

Table 10. Chemicals – Worker Exposure Limits			
Chemical	CAS No.	TVL/ACGIH (ppm)	TWA/PEL ¹ (mg/m ³)
Metaflex FCR Primer			
Propan-2-ol	67-63-0	400	999
Zinc chromates	11103-86-9	0.01 mg/m ³	0.05
Toluene	108-88-3	50	191
Isobutyl acetate	110-19-0	150	724
Butan-1-ol	71-36-3	20	STEL ² : 154 mg/m ³
Phenol	108-95-2	5	7.7 (2 ppm)
Aerodur CF Primer 37047			
2-Methoxy-1-methylethyl acetate	108-65-6	---	274
n-butyl acetate	123-86-4	150	724
Butan-2-ol	78-92-2	100	308
Aerodur Finish C21/100 UVR			
2-Methoxy-1-methylethyl acetate	108-65-6	---	274
n-butyl acetate	123-86-4	150	724

¹ TWA/PEL – Time Weighted Average / Permissible Exposure Limits (8 hours)

² STEL – Short Term Exposure Limit (15 minutes)

Ventilation is required to maintain airborne contaminants below the TLVs and

PELs. In addition, personal protective equipment is required, such as eye goggles or face shields, neoprene or polyvinyl gloves, appropriate protective clothing, and a dust filter mask or respirator.

1.7. Baseline Capital and Operating Costs

Costs with painting materials are shown in Table 11. The values include costs with painting preparation materials and painting materials (primers and topcoats). The consumption of the cleaning agent Solvent Oplosser was not recorded.

Table 11. Material Costs (Painting preparation and painting operation)	
Aircraft Model	Cost (in Euros)
Airbus A310	*
Airbus A319	6500
Airbus A340	7500

* Data not available

There is no data available for the Airbus models A321 and A340.

As to auxiliary painting materials the data available refers to an A310 aircraft, and the cost is approximately 2000 Euros. The auxiliary painting materials are, for example, plastic foils used in masking, tapes, window protectors, gloves, etc.

TAP Maintenance and Engineering conducts the aircraft maintenance work in three Hangars. Figure 3 shows Hangars 4, 5 and 6 with a total covered surface of 26380 m².

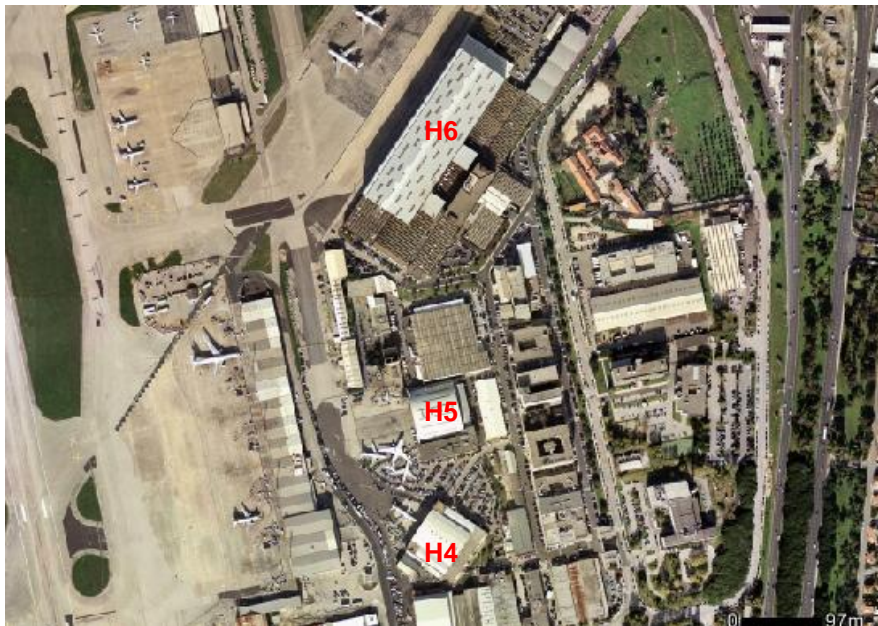


Figure 3. Aerial photograph of TAP Maintenance and Engineering. Location of

Hangars 4, 5 and 6.

Concerning power costs TAP-ME conducted a study for the painting costs in Hangar 5 and 6. These Hangars are not exclusively dedicated to aircraft painting and the data collected is affected with some inaccuracy. Regarding Hangar 6 the power consumption includes the following:

- Diesel oil for air heaters;
- Natural gas consumed at the central for hangar heating, which also serves other building (Component Shop);
- Electrical energy for electric outlets, equipment, illumination lines and compressed air.

Power consumptions within Hangar 6 (Airbus A310 aircraft painting case) are shown in Table 12.

Table 12. Power costs – Hangar 6			
Situation	Day of the week	Season	Cost (Euros/day)
Painting	Weekend	Winter	2950
Without work	Weekend	Winter	1750
Maintenance	Monday to Friday	Winter	4450
Maintenance	Monday to Friday	Summer	3900

Table 13 presents the Hangar 5 power costs (Boeing 737 aircraft painting case).

Table 13. Power costs – Hangar 5			
Situation	Day of the week	Season	Cost (Euros/day)
Painting	Weekend	Winter	2375

The manpower costs are indicated in Table 14. The values are based on Heavy Maintenance manpower costs (values of the year 2005).

Table 14. Manpower Costs for several aircraft models			
Model	Description	Direct Cost (Euros)	Total Cost (Euros)
Airbus A310	Stripping, Sanding and Painting the entire aircraft	113500	193000
Airbus A319	Sanding and Painting the entire aircraft	43000	73000
Airbus A320	Sanding and Painting the entire	47000	80000

	aircraft without decoration		
Airbus A320	Stripping, Sanding and Painting the entire aircraft	59000	101000
Airbus A320	Stripping, Sanding and Painting the entire aircraft (*)	73000	125000
Airbus A321	Stripping, Sanding and Painting the entire aircraft	62000	106000

(*) In this case the value of manxhour was higher because the stripper application method was different. Currently the stripper is spray applied.

The direct cost is the number of hours spent with direct coordination, painters and the auxiliary personnel. The total costs include all the described costs and other TAP Maintenance and Engineering costs, namely, equipment maintenance, power costs, cleaning, security, etc.

Table 15 expresses the costs of stripping and sanding process in an A310 aircraft (includes process auxiliary material). There is no data available for other aircraft models.

Table 15. Costs of sanding and stripping processes in an Airbus A310 aircraft		
Operation	Description	Costs (Euros)
Sanding	-	9500
Stripping and Sanding	With Turco 6776LO	18500
Stripping and Sanding	With Ardrex 2526	10500

The Ardrex 2526 stripper has been progressively replaced by Turco 6776LO because this product is less harmful for the Environment and Human Health.

2. IDENTIFIED ALTERNATIVES AND PRELIMINARY SCREENING

Table 16 presents the most viable alternatives to chromate and high-VOC coating systems, which are indicated that generate less pollution, and have less health and safety risks associated with them.

Table 16. Most Viable Alternatives to Chromate and High-VOC Coating System	
Product	Company
<i>High Solids Painting Scheme</i>	Akzo Nobel
<i>PreKote SP</i>	Pantheon Chemical

2.1. High Solids Painting Scheme – Akzo Nobel

Conventional solvent borne paints typically contain 8 to 30 percent solids. High solids paints contain an increased amount of non-volatiles, resulting in formulations that range from 40 to nearly 100 percent solids. These paint formulations use low-molecular-weight resins (500 to 2,000 as compared to 20,000 for conventional resins), which require less solvent to attain the desired application viscosity. These resins have highly reactive sites to aid in coating polymerization.

High-solids paints may be one-component or two-component systems based on acrylic, alkyd, epoxy, polyester, or urethane resins. High-solids coatings can be cured in conditions ranging from ambient air dry to a high temperature bake (above 180°C [350°F]).

The reduced solvent content in high-solids coatings presents some potential difficulties. Surface preparation is more critical because oils, greases, and other surface contaminants normally dissolved by solvents in conventional formulations may affect paint adhesion. Although some high-solids paints may be applied by conventional application techniques (e.g., air spraying, curtain coating, dip coating, electrostatic spraying, or flow coating), special equipment may be required for others, especially those approaching 100 percent solids. For high viscosity materials, it may be necessary to heat the paint to maintain a workable paint consistency, increase the pressure in spray applications, or use two component formulations and plural component equipment that meters and mixes the materials at the spray gun. Since thicker coatings do not blend as well as thinner coatings, color matching may be more complicated. In addition, the reduced solvent content may make clean-up more difficult.

Akzo Nobel High Solids Painting Scheme selected by TAP was *Aviox Advanced Series*:

1. *M790E*: for surface preparation is a water based detergent that gives improved adhesion properties, and the content of organic solvents is less than 10%.

2. *Aviox CF Primer (Tropical Conditions)*: is a two pack coating for aircraft exterior surfaces, and is a corrosion inhibitor, don't contain leads or chromates, resistant to aircraft fluids and chemicals, high solids content, and is compatible with *Aviox Finish*.
3. *Aviox Finish 77702*: is a polyurethane topcoat and a 3 component durable high gloss finish for exterior use. *Aviox Finish 77702* have extended durability and UV resistance, high solids content, resistance to aircraft hydraulic fluids and chemicals, and have a wide application window due to various activators, also have a wide range of colors available.

2.1.1. Process Description

The *High Solids Painting Scheme* is for aircraft exterior surfaces.

M790E, for surface preparation, shall be applied via the following procedure on fully stripped aircrafts or bare/stripped aluminum skins:

1. Remove heavy contamination of the surface with a solvent wash.
2. Rub the surface thoroughly with clean rags soaked with *M790E*.
3. Wipe off with a clean cloth after 10 to 20 seconds (No further rinsing or surface preparation is required).
4. Allow the surface to dry for a minimum of 4 hours to prevent water enclosure under rivets and overlaps.
5. Apply primer coating (the surface should be fully dry).

The *Aviox CF Primer (Tropical Conditions)* shall be spray applied to pretreated aluminum, after being thoroughly cleaned with Cleaner *M790E* or other.

The *Aviox Finish 77702* is compatible with the most commonly used primers, and shall be spray applied on clean primer.

2.1.2. Technical Considerations

2.1.3. Environmental Issues

Table 17 shows the list of products for aircraft painting and the respective mixing ratios.

Table 17. Products for aircraft painting and mixing ratios	
Product	Mixing ratio (in volume)
Cleaner M790E	-
Aviox CF Primer (Tropical conditions)	100 parts of Aviox CF Primer 55 parts of Hardener 93231
Aviox Finish 77702 White BAC 7067	100 parts of Aviox Finish 77702 50 parts of Hardener 90150 50 parts of Activator 99321

Table 18 describes the chemicals in Cleaner M 790E and the respective Chemical Abstracts Service registry numbers (CAS numbers).

Table 18. CAS Numbers for Cleaner M 790E	
Chemical	CAS Number
Propan-2-ol; isopropanol	67-63-0
Butan-1-ol; n-butanol	71-36-3

According with the *Aviox CF Primer* Material Safety Data Sheet (MSDS), *Aviox CF Primer* is highly flammable; reactive with oxidizing agents, strong alkalis and strong acids conducting to strong exothermic reactions; stable formulation, under recommended storage and handling conditions, with a basic pH; and partially soluble in cold water.

Aviox CF Primer shouldn't enter drains and watercourses, and the disposal is performed in accordance with the applicable regulations.

Aviox CF Primer contains substances presenting a health or environmental hazard within the meaning of the Dangerous Substances Directive 67/584/EEC, which are described in Table 19 with the respective CAS numbers.

Table 19. CAS numbers for Aviox CF Primer (TC) and Hardener 93231	
Chemical	CAS Number
Aviox CF Primer (TC)	
Acetoacetate resin	---
4-Methylpentan-2-one	108-10-1
Xylene	1330-20-7
Zinc Oxide	1314-13-2
Ethylbenzene	100-41-4
Hardener 93231 for Aviox CF Primer (TC)	

Ketimine resin	---
Amine-ketone-condensate	---
Xylene	1330-20-7
Silane, trimethoxy[3-(oxiranyl-methoxy)propyl]	2530-83-8
Ethylbenzene	100-41-4
5-Methylheptane-3-one	541-85-5

According with the *Aviox Finish 77702, white BAC 7067* Material Safety Data Sheet (MSDS), *Aviox Finish 77702* is flammable; reactive with oxidizing agents, strong alkalis and strong acids conducting to strong exothermic reactions; stable formulation, under recommended storage and handling conditions, with a neutral pH; and partially soluble in cold water.

Aviox Finish 77702 shouldn't enter drains and watercourses, and the disposal is performed in accordance with the applicable regulations.

Aviox Finish 77702 contains substances presenting a health or environmental hazard within the meaning of the Dangerous Substances Directive 67/584/EEC, which are described in Table 20 with the respective CAS numbers.

Table 20. CAS numbers for Aviox Finish 77702, white BAC 7067, Hardener 90150 and Activator 99321	
Chemical	CAS Number
Aviox Finish 77702, white BAC 7067	
n-butyl acetate	123-86-4
Polyester polyol	---
Cyclohexanone	108-94-1
Xylene	1330-20-7
Decanedioic acid, bis (1,2,2,6,6-pentamethyl-4-piperidiny) ester	41556-26-7
Acrylates/metacrylates	---
Decanedioic acid, methyl (1,2,2,6,6-pentamethyl-4-piperidiny) ester	82919-37-7
Hardener 90150	
Hexane, 1,6-diisocyanato-, homopolymer	28182-81-2
4-methylpentan-2-one	108-10-1
Hexamethylene-di-isocyanate	822-06-0
Activator 99321	
4-methylpentan-2-one	108-10-1
Pentane-2,4-dione	123-54-6
Propanoic acid, 3-ethoxy-, ethyl ester	763-69-9
Dibutyltin dilaurate	77-58-7

2.1.4. Health and Safety Issues

The Threshold Limit Values (TLV) of the chemicals of the Aviox Painting Scheme were collected from the Portuguese Norm NP 1796:2004 and from the publication Threshold Values for Chemical Substances and Physical Agents of the American Conference of Governmental Industrial Hygienists (ACGIH) (See Table 21).

Table 21. Chemicals – Worker Exposure Limits			
Chemical	CAS No.	TVL/ACGIH (ppm)	TWA/PEL¹ (mg/m³)
Cleaner M 790E			
Propan-2-ol	67-63-0	400	999
Butan-1-ol;	71-36-3	20	STEL ² : 154 mg/m ³
Aviox CF Primer (TC)			
4-Methylpentan-2-one	108-10-1	50	208
Xylene	1330-20-7	100	220
Ethylbenzene	100-41-4	100	441
Aviox Finish 77702			
n-butyl acetate	123-86-4	150	724
Cyclohexanone	108-94-1	25	10 ppm
Xylene	1330-20-7	100	220

¹ TWA/PEL – Time Weighted Average / Permissible Exposure Limits (8 hours)

² STEL – Short Term Exposure Limit (15 minutes)

Ventilation is required to maintain airborne contaminants below the TLVs and PELs. In addition, personal protective equipment is required, such as eye goggles or face shields, neoprene or polyvinyl gloves, appropriate protective clothing, and a dust filter mask or respirator. Chemicals are harmful by inhalation and in contact with skin, irritating to eyes, respiratory system and skin, toxic to aquatic organisms, and the vapors may cause drowsiness and dizziness.

2.1.5. Additional Supporting Literature

2.2. PreKote Surface Pretreatment – Pantheon Chemical

PreKote SP, from Pantheon Chemical, is a non-chromated pre-treatment for use on metal and composite substrates to enhance the bond between coatings and various surfaces. PreKote SP can be used on aluminium, steel, magnesium, titanium, CRES, galvanized surfaces, composite and plastic surfaces.

According with Pantheon Chemical PreKote SP cleans the surface to be painted while enhancing the adhesion of the coatings and improves corrosion protection. This process deposits a molecular layer that bonds to the surface of metal or composite material. This layer allows the coating, when applied, to get closer to the substrate surface creating a bond with the surface.

PreKote SP is not a conversion coating, does not permanently change the surface of the substrate, and is designed to be an integral part of the coating system.

2.2.1. Process Description

PreKote SP can be applied using different methods: manual, spray, power wash or immersion.

Immersion Process for Aluminium:

1. *Clean:* the used product is X-IT Platinum (Pantheon Chemical) at a temperature of 110°-130°F (43-54°C) and between 2 to 5 minutes.
2. *Rinse in Cold Water or De-ionized Water:* rinse during 2-5 minutes at a temperature of 110°-130°F (43-54°C).
3. *Deoxidize:* can be used any deoxidizer product and the application must be as per manufacturer recommendation.
4. *Rinse in Cold Water or De-ionized Water:* rinse during 2-5 minutes at maximum temperature of 110°F (43°C).
5. *PreKote SP:* application of PreKote SP at maximum temperature of 110°F (43°C) during 2-5 minutes without any circulation.
6. *Rinse in De-ionized Water:* rinse during 2-5 minutes at a temperature of 110°-130°F (43-54°C).
7. *Dry:* As required.

Spray Process for Aluminum:

1. *Clean:* the used product is X-IT Platinum (Pantheon Chemical) at a temperature of 110°-130°F (43-54°C) and 20-30 psi pressure during 60 sec.
2. *Rinse in Cold Water or De-ionized Water:* rinse during 60 sec at a temperature of 110°-130°F (43-54°C).
3. *Deoxidize:* can be used any deoxidizer product and the application must be

at a temperature of 110°-130°F (43-54°C) and 20-30 psi pressure during 60 sec.

4. *Rinse in Cold Water or De-ionized Water:* rinse during 60 sec at room temperature.
5. *PreKote SP:* application of PreKote SP at maximum temperature of 110°F (43°C), at a pressure of 15-20 psi during 90 sec.
6. *Rinse in De-ionized Water:* rinse during 60 sec at a temperature of 110°-130°F (43-54°C) and 15-20 psi pressure.
7. *Dry:* As required.

Aircraft Application Process:

1. *PreKote First Application:* application of PreKote SP to the surface being prepared, creating a “flood type coating”. The application must start from the top and work down. The surface must be completely scrubbed with a 180-240 grit alumina oxide pad to generate a rich lather. Start from top and work down. A pneumatic power buffer or pole scrubber may be used. Pay particular attention to leading edges and other high-erosion areas. Let PreKote dwell for approximately 2 minutes and then proceed to step 2.
2. *PreKote Second Application:* flood surface again with PreKote. The surface must be again completely scrubbed with a 180-240 grit alumina oxide pad to generate a rich lather. Start from top and work down.
3. *Water Rinsing:* rinse the aircraft thoroughly and allow drying. The aircraft is ready for primer and paint application.¹

¹Note: If the aircraft is exposed to significant airborne contamination prior to priming/painting, all surfaces should be wiped down with a clean, PreKote moistened, lint-free cloth.

2.2.2. Technical Considerations

PreKote SP has been subject to laboratory tests over the last eight years.

PreKote was approved for use on the F-16, of USAF, in 1998. In 2003, use of PreKote was mandated by the Air Education and Training Command (AETC) of the USAF.

The next tables present tests that verify acceptable performance of chemical conversion coatings as Group 2 coatings. This group represents painted surfaces requiring maximum paint to substrate adhesion. Group 2 chemical conversion coatings increase adhesion on parts requiring paint or primer for end use that normally exhibit poor adhesion on the bare substrate.

General Requirements

Table 22. General Requirements Tests for Group 2 Coatings		
Test	Results	Reference
Reparability/ Compatibility	Pass	Boeing Seattle, Paint Softening, D6-17487/ASTM F502
Humidity Resistance	Pass	Boeing Seattle BMS10-11, Test 24. 8.2.16 HUMIDITY Use three or more Class C panels. The panels shall be suspended in a humidity cabinet in accordance with BSS7250. The cabinet shall operate at $120^{\circ} \pm 1.8^{\circ}\text{F}$ with condensing humidity conditions [for 32 days]. Panel evaluation after exposure shall include adhesion in accordance with Section 8.2.8. Class C panels = 4 by 6 by 0.020 inch bare 2024-T3 aluminum alloy in accordance with QQ-A-250/4 with conversion coating in accordance with BAC5719, Type I, Class A. These are the only panels that should be non-clad aluminum. **Note** – Clad panels were substituted in lieu of bare panels to account for the difference between the interior and exterior fuselage skins (the condensing humidity test is currently called out in BMS10-11)

Adhesion Requirements

Table 23. Adhesion Requirements Tests for Group 2 Coatings		
Test	Results	Reference
Wet Tape Adhesion	Pass	Boeing Seattle BMS10-72, Test 16. Scribe Adhesion (Wet and Dry) 8.2.10.2 Cross-Hatch Test (3 panels 2024-T3/PreKote™, 3 panels 2024-T3/Alodine 1000L, 3 panels 7075-T6/PreKote™, 3 panels 7075-T6/Alodine 1000L) Prepare test panels in accordance with Section 8.1 and cure for 7 days minimum. 1. Subject the panels to fluid immersion, when required. Wipe panels dry with clean dry cheesecloth after tests. Procedure: (1) Test in accordance with BSS7225, Type I, Class 5 and Type III, Class 5. (2) Examine panel for film failures. Check tape for film removal. (3) A retest is required if a primer adhesion failure occurs.
	Pass	ESCTP Phase 1 Report, <u>Nonchromated Aluminum Pretreatments</u> , Project #PP025, Pgs 29-39
	Pass	<u>Non-Chromate Pre-treatments vs. Non-Chromate Primers Final Report</u> Contract No. F42620-00-D-0039-0001, UDRI Tracking No. UDRI-2187-F2-02. Pg 7, 8
Flexibility (Ambient Impact; Low Temperature)	Pass	<u>Non-Chromate Pre-treatments vs. Non-Chromate Primers Final Report</u> Contract No. F42620-00-D-0039-0001, UDRI Tracking No. UDRI-2187-F2-02. Pg 14, 15 Ambient Temperatures

Corrosion Resistance Requirements

Table 24. Corrosion Resistance Requirements Tests for Group 2 Coatings		
Test	Results	Reference
Salt Spray	Pass	Boeing Seattle BMS10-72, Test # 20 a. – 3000 hour Salt Spray (3 panels 2024-T3/PreKote™, 3 panels 2024-T3/Alodine 1000L, 3 panels 7075-T6/PreKote™, 3 panels 7075-T6/Alodine 1000L) 8.2.14.1 Salt Spray <ol style="list-style-type: none"> 1. Prepare test panels in accordance with Section 8.1 and cure for 7 days minimum. 2. [Machine] Scribe two diagonal marks from corner to corner through the coating down to the base metal. 3. Expose test panels to 3000 hours minimum of 5 percent salt spray fog in accordance with BSS7249, except place panels on an incline of 6 degrees from vertical (painted side up). 4. Examine the test panel for corrosion. Conduct adhesion test in accordance with 8.2.10.1.
	Pass	ESCTP Phase 1 Report, <u>Nonchromated Aluminum Pretreatments</u> , Project #PP025, Pgs 54, 3000 hrs, ASTM B117, Navair, Patuxent River, MD, AL2024 w/Mil-PRF-23377or 85582Cl2 primer.
	Pass	<u>Non-Chromate Pre-treatments vs. Non-Chromate Primers Final Report</u> Contract No. F42620-00-D-0039-0001, UDRI Tracking No. UDRI-2187-F2-02. Pg 9, 10
SO ₂ /Salt	Pass	ESCTP Phase 1 Report, <u>Nonchromated Aluminum Pretreatments</u> , Project #PP025, Pgs 59-61, ASTM G85 Annex 4, Navair, Patuxent River, MD, AL2024 w/Mil-PRF-23377or 85582Cl2 primer
Filiform	Pass	<u>Non-Chromate Pre-treatments vs. Non-Chromate Primers Final Report</u> Contract No. F42620-00-D-0039-0001, UDRI Tracking No. UDRI-2187-F2-02. Pg 13
	Pass	Boeing Seattle BMS10-72, Test # 20 b. Filiform Corrosion, Machined Scribe (3 panels 2024-T3/PreKote™, 3 panels 2024-T3/Alodine 1000L, 3 panels 7075-T6/PreKote™, 3 panels 7075-T6/Alodine 1000L) 8.2.14.2 Filiform Corrosion <ol style="list-style-type: none"> 1. Prepare test panels in accordance with Section 8.1, except dry film thickness of enamel shall be 4.0 ± 0.5 mils. 8.2.14.2 Filiform Corrosion 2024–T3 Clad Aluminum 4 × 6 × 0.040 inch 2. Machine two diagonal lines to the base metal in accordance with BSS7258, Type I. 3. Expose panels in accordance with BSS7258 for 30 days minimum. 4. Examine panels for corrosion, blisters, and other film failures.

Fluids Resistance Requirements

Table 25. Fluids Resistance Requirements Tests for Group 2 Coatings		
Test	Results	Reference
Fluid Resistance	Pass	<u>Non-Chromate Pre-treatments vs. Non-Chromate Primers Final Report</u> Contract No. F42620-00-D-0039-0001, UDRI Tracking No. UDRI-2187-

		F2-02. Pg 7
Fuels Resistance	Pass	Non-Chromate Pre-treatments vs. Non-Chromate Primers Final Report Contract No. F42620-00-D-0039-0001, UDRI Tracking No. UDRI-2187-F2-02. Pg 7

Marine Atmospheric Test on Scribed Painted Substrates Requirement

Table 26. Marine Atmospheric Test on Scribed Painted Substrates Requirement Tests for Group 2 Coatings		
Test	Results	Reference
Beach Test, NASA, Kennedy Space Center, FL	Pass	ESCTP Phase 1 Report, <u>Nonchromated Aluminum Pretreatments</u> , Project #PP025, Pgs 84, 12 months Exposure AL2024 w/Mil-PRF-23377or 85582C12 primer.

Rain Erosion Requirement

Table 27. Rain Erosion Requirement Test for Group 2 Coatings		
Test	Results	Reference
Boeing Seattle	Pass	BMS10-72, Test #23 - Rain Erosion Use all 8 rain erosion foils, 4 foils have PreKote™ and 4 foils have Alodine 1000L. 1. Immerse foils in water at 75 ±5 F for 16 to 24 hours just prior to test. Start test within 1 hour maximum after removal from water. 2. Expose specimens to 385 miles per hour (at specimen midpoint) with 3 to 4 inches per hour water spray (1 to 4 mm drop size) for 30 minutes set time. Check and measure erosion peeling from paint leading edges

2.2.3. Environmental Issues

According with the PreKote Material Safety Data Sheet (MSDS), PreKote is water-based, biodegradable, non-toxic, non-hazardous, non-flammable, non-corrosive and stable formulation with a pH range from 10.0 to 11.5. The MSDS also lists the health hazardous from exposure to PreKote as slight and the flammability, reactivity and contact hazards as insignificant.

The ingredients Diethylene Glycol Monobutyl Ether, <3%, CAS No. 112-35-5 and N-Methylpyrrolidone (NMP), <3%, CAS No. 872-50-4; are contained in the formulation and is subject to reporting requirements under SARA Title III Section 313 Part 372. All other ingredients are on the TSCA Inventory.

2.2.4. Health and Safety Issues

Personal protective goggles must be utilized. It is not necessary to have respiratory and ventilation control measures.

Nevertheless, avoid prolonged contact with skin and wash after handling.

2.2.5. Additional Supporting Literature

- Air Education and Training Command, July 1999, *AETC Test Project: Surface Conversion Coating – Qualification Operational Test and Evaluation Final Report*, Randolph Air Force Base, Texas.
- Buchi, Richard H.; Patterson, Ken; Gowers, Clyde J.; *Non-Chromate Conversion Coating – Final Report*; Ogden Air Logistics Center Science and Engineering Laboratory, 3 April, 1998.
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- United States Environmental Protection Agency (EPA); *Regulatory Determination for the PreKote Surface Preparation Process*; Washington, D.C., 1 April, 2003.
- Roberts, Laura; Galanis, Anthony; *Proven Non-Chromated Technology*; Pantheon Chemical.
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- Christopher A. Joseph; *Non-Chromate Pre-Treatments vs. Non-Chromate Primers – Final Report*; University of Dayton Research Institute (UDRI), 17 March, 2003, Dayton, OH.
- Material Safety Data Sheet (MSDS) on PreKote Surface Treatment, Pantheon Chemical, May 2004.
- Boeing Commercial Airline Approval Letter on PreKote Surface Treatment, 22 April, 2004.
- PreKote SP Immersion and Spray Application Process for Aluminum, Pantheon Chemical.